



ELASTIC PROPERTIES OF THE INTERMETALLIC COMPOUND ReSi_2

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(Received September 26, 1997)

(Accepted October 27, 1997)

Introduction

The binary Re-Si and ternary Mo-Re-Si systems have been of interest for a number of reasons: occurrence of superconductivity in Re-rich Re-Si solid solutions [1], potential applications of ReSi_2 and $(\text{Mo}_x\text{Re}_{1-x})\text{Si}_2$ alloys in infrared detectors [2], and use of Re as an alloying element to MoSi_2 [3,4] which is a potential high temperature structural material [5]. Early investigations found that the intermetallic compound ReSi_2 had a body-centered tetragonal C11_b (MoSi_2 -type) structure with lattice parameters of $a = 0.3132$ nm and $c = 0.7681$ nm [1,6]. The alloy was reported to melt congruently at $\sim 1940^\circ\text{C}$ and have a composition of $\text{ReSi}_{1.8}$ with vacancies on Si sites [1]. $(\text{Mo}_x\text{Re}_{1-x})\text{Si}_2$ alloys formed a continuous range of solid solutions with the MoSi_2 structure [6]. Later, Siegrist *et al.* [7] reported a body-centered orthorhombic structure with $a = 0.3128$ nm, $b = 0.3144$ nm and $c = 0.7677$ nm (space group *Immm*) but found the composition close to ReSi_2 . More recent investigations by Gottlieb *et al.* [8] report the stoichiometry to be $\text{ReSi}_{1.75}$ and an orthorhombic unit cell with $a = 0.3139$ nm, $b = 0.3121$ nm and $c = 0.7670$ nm, and $\alpha = 89.87^\circ$ which indicates a very weak monoclinic distortion as well. Since ReSi_2 is a semiconductor with a band gap of ~ 0.2 eV [7], stoichiometry of $\text{ReSi}_{1.75}$ would result in an even number of valence electrons of Re and Si as expected for a semiconductor [8].

Structural properties are crucial for understanding deformation behavior of a solid, e.g., dislocation slip systems, twinning modes, etc. A knowledge of elastic constants is essential for many practical applications related to the mechanical properties of a solid: load-deflection, thermoelastic stress, internal strain (residual stress), sound velocities, dislocation core structure, and fracture toughness. Further, the elastic properties may provide insight on the atomic bonding and resistance to deformation by shear [9]. In this investigation, the elastic properties of ReSi_2 were evaluated using resonant ultrasound spectroscopy (RUS) and are compared to the elastic properties of other transition metal disilicides.

Experimental Procedures

Arc-melted buttons of ReSi_2 were prepared in an argon atmosphere using elemental Re and Si with nominal purities of 99.999 at.%. The buttons were turned over and remelted 5–6 times to ensure homogeneity. For the elastic constant measurements, the polycrystalline ReSi_2 specimen was cut into

a rectangular parallelepiped with dimensions $a = 2.004 \pm 0.002$ mm, $b = 3.082 \pm 0.001$ mm, and $c = 3.904 \pm 0.001$ mm. The mass-density of the specimen determined from its dimensions and mass was 9.3437 g/cm^3 .

The elastic constants of a material can be determined in various ways. We determined the elastic constants of the polycrystalline ReSi₂ from its resonant frequencies using a RUS technique [10]. The advantages of RUS as compared with conventional ultrasonic methods for measuring elastic constants and the details of the experimental set up have been discussed elsewhere [9].

Using the method described by Migliori et al. [10], we can easily calculate resonant frequencies of a solid from its elastic constants, dimensions, and mass density. Since no analytical method exists, we have to solve the inverse problem numerically to determine elastic constants from resonant frequencies in the following way: first, we estimate the elastic constants as closely as possible from other sources. For the present study, we start with the c_{11} and c_{44} of polycrystalline MoSi₂, which are as follows: $c_{11} = 464$ GPa and $c_{44} = 191$ GPa [9]. Then we calculate the resonant frequencies using the estimated elastic constants, the dimensions and the mass density of the specimen. Second, we define a figure of merit:

$$F = \sum_{i=1}^N w_i (f_i - g_i)^2 \quad (1)$$

where g_i and f_i indicate the i -th measured and calculated frequencies, respectively; N denotes the total number of measured frequencies; and w_i is a weighting factor chosen (usually either 0 or $1/g_i^2$ so that F is a measure of fractional deviation) to reflect the degree of confidence in the measured frequency g_i . Finally, we use the Levenberg-Marquardt method [11] as a systematic scheme to locate the minimum of F in a multidimensional elastic-constant space (a two-dimensional space in this case because of the elastic isotropy of the polycrystalline specimen). We estimate the accuracy of the elastic constants c_{ij} by considering the shape of the surface F near the minimum. F is assumed to be a quadratic function of the elastic constants in this neighborhood, so that the surfaces of constant F are ellipsoid with major axes related to the accuracy with which the corresponding elastic constants are determined. We estimate the accuracy for each c_{ij} by finding the length of the corresponding semi-major axis of the ellipsoid when F exceeds the minimum by 2%.

For isotropic symmetry, the two independent c_{ij} are usually chosen to be c_{11} and c_{44} . Using the following relationship for the isotropic ReSi₂ specimen, we obtain four practical elastic constants (shear modulus G , Young's modulus E , bulk modulus K and Poisson's ratio ν) from its c_{11} and c_{44} :

$$G = c_{44} \quad (2)$$

$$E = c_{44}(3c_{11} - 4c_{44})/(c_{11} - c_{44}) \quad (3)$$

$$K = 1/3(3c_{11} - 4c_{44}) \quad (4)$$

$$\nu = 1/2(c_{11} - 2c_{44})/(c_{11} - c_{44}) \quad (5)$$

Results and Discussion

Light microscopy indicated that the grain size was $\sim 100 \text{ }\mu\text{m}$ and the alloy contained $\sim 5 \text{ vol.}\%$ of excess Si, suggesting that the Re/Si ratio in this compound is less than 2 (for convenience, rhenium disilicide is designated by the formula ReSi₂ in this paper). No microvoids or cracks were observed in the arc-melted buttons. An optical micrograph of as-cast ReSi₂ is shown in Fig. 1. X-ray powder

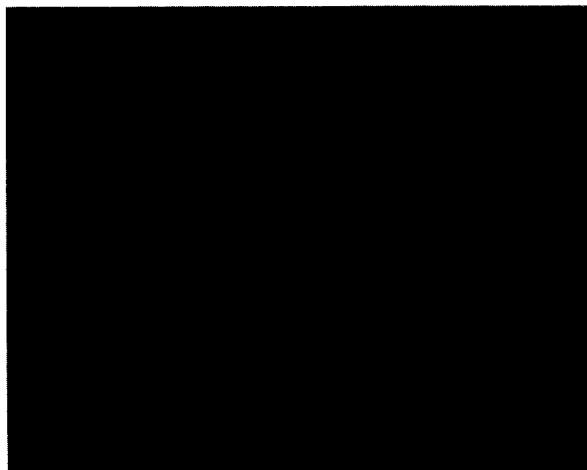


Figure 1. Optical micrograph showing the microstructure of cast ReSi_2 .

diffraction indicated an orthorhombic distortion of the C11_b MoSi_2 -type structure. The details of the characterization of the structure by X-ray diffraction and transmission electron microscopy will be presented elsewhere.

In the RUS experiment, more than 40 resonant peaks between 0.40 MHz and 1.55 MHz were employed to obtain the isotropic elastic constants. Figure 2 shows a portion of the resonant-frequency spectrum for the polycrystalline ReSi_2 specimen at room temperature from 1.0 to 1.2 MHz. The data fitting for the 6 resonances of ReSi_2 shown in Fig. 2 where F reaches minimum is shown in Table 1. The r.m.s. error for the fitting of all 40 resonance peaks in the range from 0.40 MHz to 1.55 MHz is less than 0.6%, which indicates a good agreement between the measured and calculated resonances.

The isotropic elastic moduli and Poisson's ratio as calculated from Eqs. (2–5) from measured c_{11} and c_{44} values for ReSi_2 are $K = 165$ GPa, $E = 344$ GPa, $G = 149$ GPa, and $\nu = 0.1536$, respectively. They are compared with the elastic properties of constituent elements Re and Si (taken from [12]) in Table 2. E , G and K of ReSi_2 are lower than those of pure Re but significantly higher than those of Si. Further, the Poisson's ratio of ReSi_2 is substantially smaller than that of Re and Si, indicating a stronger bonding directionality in the intermetallic compound.

The isotropic elastic moduli of ReSi_2 are compared with those of other transition metal disilicides in Table 3. It can be seen from Table 3 that the Young's moduli of C11_b -based transition metal

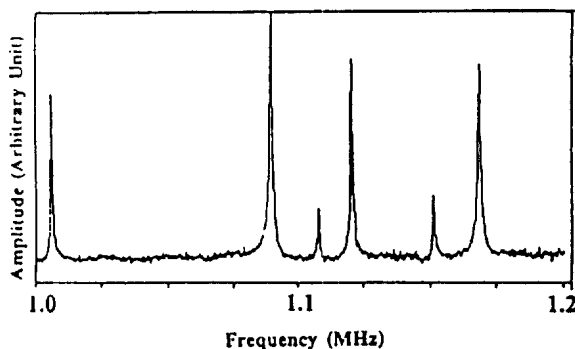


Figure 2. A portion of room temperature resonant-frequency spectrum of ReSi_2 .

TABLE 1
A Portion of Measured and Calculated Resonant Frequencies of
the ReSi₂ Polycrystal. f_{measured} is the Measured Frequency and
 $f_{\text{calculated}}$ the Calculated Frequency.

f_{measured}	$f_{\text{calculated}}$	Error (%)
1.006000	1.005363	-0.06
1.089400	1.083402	-0.55
1.107500	1.112477	0.45
1.120300	1.122732	0.22
1.151100	1.165066	1.21
1.168500	1.170332	0.16

disilicides (including ReSi₂ which only has a small orthorhombic distortion from C11_b) increase slightly with increasing melting point, but for C40 disilicides the Young's moduli are about the same for different compounds with melting points ranging from 1490°C to 2200°C. It can also be seen from Table 3 that the K/G ratios of the C11_b-based transition metal disilicides are close to 1.1 and vary from 1.12 to ~1.25 for the C40 disilicides. Based on the Pugh criterion [13], alloys with high K/G ratios may be expected to be ductile and hence, the ductility of ReSi₂ is not expected to be significantly different from MoSi₂ or WSi₂. Table 3 indicates that the Poisson's ratios of C11_b-based disilicides are close to 0.15, which is much smaller than those of common metals and alloys (0.33). This suggests that the C11_b-based transition metal disilicides have strong directional interatomic bonding, because a low Poisson's ratio is an indication of less bonding isotropy. However, the most striking feature in Table 3 is that the isotropic elastic moduli of ReSi₂ are substantially lower than those of MoSi₂ and WSi₂, and closer to the C40 disilicides than to the C11_b disilicides. This may be due to the structural distortion, the off-stoichiometric composition and/or the presence of Si second phase (~5% by volume) in the ReSi₂ alloy. For example, the orthorhombic distortion (~0.5%) can change the Re-Si interatomic distances as compared to MoSi₂ and WSi₂ [7] and Re-rich off-stoichiometric composition may result in partially filled Si sites [8], thereby influencing the interatomic bonding in this compound. The Debye temperature (θ_D) of ReSi₂ was calculated to be 562 K from the elastic constants by the approach presented in ref. [9], and is compared to the θ_D of other transition metal disilicides in Table 3. The θ_D of ReSi₂ is about the same as that of TaSi₂ but lower than other disilicides due to the relatively higher mass density and lower shear modulus.

Conclusions

1. The room temperature elastic parameters of ReSi₂ have been measured using the resonant ultrasound spectroscopy technique. The shear, bulk, and Young's moduli of ReSi₂ are 149, 165, and 344 GPa, respectively.

TABLE 2
Room Temperature Isotropic Elastic Moduli and Poisson's Ratios of ReSi₂
and its Constituent Elements.

Materials	K (GPa)	E (GPa)	G (GPa)	ν
Re*	334	466	181	0.26
Si*	98	163	68	0.22
ReSi ₂	165	344	149	0.15

*: from Ref. [12].

TABLE 3
Room Temperature Isotropic Elastic Properties and Melting Points of Some Transition Metal Disilicides.

Materials	Crystal structure	Melting point (°C)	K (GPa)	E (GPa)	G (GPa)	ν	Debye T (K)
ReSi ₂	ortho-rhombic	1940	165	344	149	0.154	562
*MoSi ₂	tetragonal C11 _b	2020	210	440	191	0.151	759
*WSi ₂	tetragonal C11 _b	2324	222	468	204	0.149	625
*CrSi ₂	hexagonal C40	1490	172	355	153	0.156	793
*VSi ₂	hexagonal C40	1677	167	343	148	0.158	791
NbSi ₂	hexagonal C40	1920	191	363	153	0.184	688
*TaSi ₂	hexagonal C40	2200	192	359	151	0.189	552

*: data for all materials other than ReSi₂ are taken from Chu *et al.* [9]

2. The bulk modulus of ReSi₂ is close to the average values derived from the rule of mixtures but the shear and Young's moduli are larger than those obtained from the rule of mixtures.
3. The room temperature Poisson's ratio of ReSi₂ is 0.15 which is similar to those of other C11_b-based transition metal disilicides, suggesting a strong bonding directionality in these intermetallics.
4. Room temperature moduli of ReSi₂ are significantly lower than those of the C11_b MoSi₂ and WSi₂ compounds, even though the ReSi₂ structure only has a small orthorhombic distortion from the C11_b structure.

Certainly, further detailed studies are required to investigate the elastic properties of single crystal ReSi₂, involving a combination of single crystal growth, experimental measurements and theoretical calculations. Also, it is important to compare the mechanical properties of ReSi₂ and MoSi₂ in light of the apparent differences in their elastic parameters. These studies are under way.

Acknowledgments

This research was performed under the auspices of the United States Department of Energy, Office of Basic Energy Sciences.

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